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STORAGE-STABLE CONTACT ADHESIVE BASED ON AN AQUEOUS POLYURETHANE
DISPERSION OR SOLUTION
[LAGERSTABILER KONTAKTKLEBSTOFF AUF BASIS EINER WÄSSRIGEN DISPERSION ODER
LÖSUNG EINES POLYURETHAN]

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The invention relates to a storage-stable contact adhesive based on an aqueous dispersion or solution of polyurethane, as well as to its manufacturing.

Today, contact adhesives are still predominantly solvent-based adhesives that are applied in liquid form to the two substrates to be glued and after extensive evaporation of the solvent (flash-off time), i.e. when the adhesive films are apparently dry, are capable for a certain period of time (open time) of leading to a high initial strength (immediate strength) in a relatively short period of time with the effect of pressure. These initial or even immediate strengths increase in the course of storage until the final strengths are achieved after hours or days. Therefore the contact adhesive can be used over large surfaces, without additional fastening of the substrates, and because of their unique combination of properties are often the only possible way to glue two impermeable materials having large surfaces so immediate strength is achieved.

Basic polymers are mainly polychloroprene, nitrile or styrene/butadiene rubber and polyurethanes. The contact adhesives often additionally contain so-called tackifiers of resins such as colophonium, hydrocarbon or phenol resins. Because of the problem of organic solvents, increasingly attempts have been made to convert the contact adhesives /2 to aqueous systems.

Water-based contact adhesives have been known to the person skilled

* Numbers in the margin indicate pagination in the foreign text.

in the art for many years. For reasons of environmental and consumer protection, they are welcome alternatives to solvent-based products. The strength spectrum of water-based contact adhesives is generally clearly lower than the analogous solvent-based products. This is especially true for water resistance. For example, natural leather latexes, dispersions of copolymerides of vinyl acetates, polychloroprene dispersions, acrylate dispersions or polyvinylidene chloride dispersions can be considered as the polymer basis of water-based contact adhesive. Polyurethane dispersions are also known to the person skilled in the art that briefly become tacky on contact starting at approx. 50°C and that are especially used for thermo-activated sole gluing on shoes. These types of adhesives usually have a low heat resistance (less than 70°C). In addition, they have the following disadvantages: they additionally require instruments for heat activation, cannot be used on surfaces of any desired size and therefore are only conditionally accepted by people in the trades.

The object of the invention is to provide a storage-stable contact adhesive based on aqueous dispersions or solutions, which after the flash-off times that are usual in practice (15 to 45 minutes) and open times (15 to 90 minutes), lead to high initial and final strengths connected with an adequately high heat resistance ($\geq 70^{\circ}\text{C}$).

DE-OS 25 58 653 describes an aqueous dispersion of polyurethane containing silanol for increasing the oil and water deflecting effect /3 of a porous substrate like textile or leather. Films produced from them can also be randomly tacky in an unpredictable way. Thus Example 4 describes a polyurethane dispersion of toluene diisocyanate, polyoxypropylene diol

with an average molecular weight MW_n of 4000, the triethylamine salt of α -bis(hydroxymethyl)propionic acid and triethoxysilylpropylamine. The films formed thereof are soft and tacky. They can be used to connect glass plates or plastic to glass.

The known dispersions are generally stable at room temperature and within a pH range of about 6.5 to 9. The cross-linking is considerably accelerated by acid and base catalysts. Advantageously they are carried out in 5 to 60 seconds at 75 to 200°C (see page 18, last paragraph, to page 19, first paragraph).

This is obviously a case of contact adhesive, i.e. an adhesive that is applied on one side and leads to a permanently tacky film to which a second substrate adheres with low strength after slight pressure.

The teaching of DE-OS 25 58 653 is taken up and continued in EP 315 006. It describes a storage-stable cationically modified polyurethane that dries to cross-linked films having aqueous solutions or dispersions of alkoxysilane groups. They can then be stored if the pH value is from 3 to 6. The content of alkoxysilane compounds will be at least 1.3 weight-%, calculated as SiO_3 . The dispersion leads to hard and elastic coatings. It is especially suitable for paint manufacturing (see page 8, lines 1 to 14). This is not to speak of tackiness, rather, it is absolutely necessary for the paint formulation that the films are free of /4 tackiness and blocking in the shortest possible time in order to prevent e.g. adherence of dust.

After modification and selection of characteristics of the teachings described above in the area of coatings, the contact-tacky property of

aqueous dispersions or solutions of a cationically-modified, alkoxysilane-terminated polyurethane has been discovered and used as the basis for achieving the object set.

The solution according to the invention can be found in the patent claims.

A contact adhesive is thus considered storage-stable if at room temperature (23°C), it is present after 1 year without noticeable changes in viscosity or properties.

Suitable isocyanates (component a) are any organic compounds that have more than one, and especially 2, isocyanate groups on the average.

Preferably diisocyanates $Q(NCO)_2$ are used, whereby Q is an aliphatic hydrocarbon radical with 4 to 12 carbon atoms, a cycloaliphatic hydrocarbon radical with 6 to 15 carbon atoms, an aromatic hydrocarbon radical with 6 to 15 carbon atoms or an araliphatic hydrocarbon radical with 7 to 15 carbon atoms. Examples of these diisocyanates that are preferably used include tetramethylene diisocyanate, hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,4-diisocyanato-cyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methyl cyclohexane, 4,4'-diisocyanato-dicyclo hexylmethyl, 4,4'-diisocyanato-dicyclo hexylpropane (2,3), 1,4-diisocyanato-benzene, 2,4-diisocyanato-toluene, 2,6-diisocyanato-toluene, 4,4'-diisocyanator-diphenyl /5 methane, p-xylylene diisocyanate and mixtures developed from these compounds.

Aliphatic diisocyanates, especially m- and p- tetramethyl xylene diisocyanate (TMXDI) and isophoron diisocyanate are preferred. It is

naturally also possible to additionally use higher-function polyisocyanates known in polyurethane chemistry or modified, e.g. carbodiimide groups, allophanate groups, isocyanurate groups, urethane groups and/or biuret groups that are also known.

The polyol b) is understood as a compound with two or more aliphatic OH groups in the molecule. For the invention claimed, any polyether, polyester, polyether ester, polycarbonate or polyacrylate polyol in the molecular weight range 100 to 8000, and preferably 500 to 3000 of the type known from polyurethane chemistry is preferred. Any mixtures of these types of polyhydroxyl compounds can also be used. Preferably, polyether polyols or polyester polyols of the known molecular weight range are used as component b), especially polyether polyols that have 2 to 3 alcoholic hydroxyl groups as a statistical average. The manufacturing of these initial materials is part of the state of the art and is described, for example in the plastic manual, Vol. VII, "Polyurethane," Carl Hanser Verlag Munich (1966), pages 45 ff. Concrete examples for component b) include polypropylene glycols, polytetrahydrofuran, polyethylene glycols and their mixed polymers. Polyols with amine end groups can also be considered. The molar ratio of component a) to component b), whereby in this calculation for component b) the components containing tertiary amine groups necessary for dispersion are also included, is 0.8:1 to 1.8:1, and preferably /6 1.1:1 to 1.6:1.

As tertiary amine compounds c), any hydroxy and/or amino functional monofunctional, and especially bifunctional compounds are suitable that are in the molecular weight range 88 to 1000, and preferably 89 to 300,

and have tertiary amine nitrogen atoms, the tertiary nitrogen atoms of which can be transferred at least partially into tertiary and/or quaternary ammonium groups during or after the end of the isocyanate polyaddition reaction. These include, for example, compounds like 2-(N,N-dimethylamino) -ethylamine, N-methyl- diethanolamine, N-methyl-diisopropanolamine, N-ethyl-diethanolamine, N-ethyl-diisopropanolamine or N'N'-bis-(2-hydroxyethyl)-perhydropyrazine N-methyl-bis-(3-aminopropyl)-amine, N-methyl-bis(2-aminoethyl)-amine or N,N',N''-trimethyl-diethylene triamine, N,N-dimethyl aminoethanol, N,N-diethylamino ethanol, 1-N,N-diethylamino-2-aminoethane and 1-N,N-diethylamino-3-aminopropane.

The quantity of component c) is measured in such a way that polyurethane is dispersed in water so it is white or is soluble so it is clear. Preferably 2 to 200, and preferably 2 to 100, per 100 g polyurethane of ammonium groups must be present.

The alkoxysilane compounds d) to be used according to the invention involve compounds of the general formula $X-Si(OR)_yH_z$, whereby y stands for 2 or 3, z stands for 1 or 0, H stands for hydrogen or an alkyl radical with 1 to 6 C atoms, X stands for an organic radical, which contains at least one group that can react with isocyanate groups, preferably a hydroxyl or primary amino group, and R stands for the same or different radicals from the following group: hydrogen and preferably alkyl group with 1 to 4 C atoms. /7

Preferably R stands for methyl and/or ethyl radicals and X stands for a 2-hydroxyethyl, 3-hydroxy-propyl, 2-(2-hydroxyethoxy)-ethyl-2-(2-amino ethylamino)-ethyl- or 3-(3-aminopropylamino)-propyl radical.

Examples of suitable and/or preferred initial materials d) include

$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{C}_2\text{H}_5-\text{CH}_3)_3$, $\text{HO}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$,
 $\text{HO}-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{CH}_3)_3$, $\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$,
 $(\text{HO}-\text{C}_2\text{H}_4)_2-\text{N}-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{CH}_3)_3$,
 $\text{HO}-(\text{C}_2\text{H}_4-\text{O})_3-\text{C}_2\text{H}_4-\text{N}(\text{CH}_3)-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{C}_4\text{H}_9)_3$,
 $\text{H}_2\text{N}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{Si}(\text{O}-\text{CH}_3)_3$, $\text{HS}-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{CH}_3)_3$,
 $\text{H}_2\text{N}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OC}_2\text{H}_5)_3$, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-(\text{CH}_2)_2-\text{Si}(\text{O}-\text{CH}_3)_3$,
 $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OC}_2\text{H}_5)_3$, $\text{HO}-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$,
 $\text{HO}-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{C}_2\text{H}_5)_3$, $\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$,
 $(\text{HO}-\text{C}_2\text{H}_4)_2-\text{N}-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{C}_2\text{H}_5)_3$, $\text{H}_2\text{N}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{Si}(\text{O}-\text{C}_2\text{H}_5)_3$,
 $\text{HS}-(\text{CH}_2)_3-\text{Si}(\text{O}-\text{C}_2\text{H}_5)_3$, $\text{H}_2\text{N}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OC}_2\text{H}_5)_3$,
 $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-(\text{CH}_2)_2-\text{Si}(\text{O}-\text{C}_2\text{H}_5)_3$, $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{OC}_2\text{H}_5)_3$

Instead of an OR substituent, an H or an alkyl radical of C_1-C_6 can also occur.

The alkoxysilanes d) are used in a quantity such that in the resulting polyurethane less than 3.0 and preferably 0.1 to 1.3 weight-% - calculated as SiO_3 and related to the weight of polyurethane - is incorporated.

A chain-lengthening compound (component e) can also be used in a 1/8 concentration from 0 to 20 weight-%, related to the polyurethane weight. This involves either organic, preferably bivalent and/or trivalent and specially bivalent polyhydroxy compounds with molecular weight range 62 to 399 and preferably 62 to 250, or amine or hydrazine chain-lengthening compounds and/or cross-linkers in the molecular weight range 32 to 399 and preferably 60 to 250.

The first-named representatives of the structural components e)

include, for example, simple multivalent alcohols like ethylene glycol, propylene glycol, propane diol-(1,3), butane diol-1,4, hexane diol-1,6, trimethylol propane or glycerin. Lower-molecular polyester diols, e.g. adipinic acid-bis-(hydroxyethyl)-ester or low-molecular diols containing ether groups like diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol or tetrapropylene glycol can also be used as structural components e). Components bearing carboxyl groups or containing sulfonic acid groups may be used up to a concentration of max. 3 weight-% as structural components. Dimethylol propionic acid is a preferred representative.

Included in the last-named compounds are e.g. ethylene diamine, hexamethylene diamine, piperazine, 2,5-dimethyl piperazine, 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane (isophorondiamine, IPDA), 4,4'-diamino dicyclohexylethane, 1,4-diamino cyclohexane, 1,2-diamino propane, hydrazine, hydrazine hydrate, amino acid hydrazide, e.g. 2-amino acetic acid hydrazide or bis-hydrazide, e.g. succinic acid-bis-hydrazide.

In particular, the amine and/or hydrazine chain-lengthening compounds that have no tert. nitrogen can also be used in the method according to the invention in blocked form, i.e. in the form of the /9 corresponding ketimines (DE-AS 27 25 589), ketazine (DE-OS 28 11 148, US-PS 4 269 748) or amine salts (US-PS 4 292 226). Also oxazolidine, as it is used e.g. according to DE-OS 27 32 131 and/or US-PS 4 192 937, represents capped diamines that can be used in the method according to the invention analogously to the named prior publications for chain

lengthening of the NCO prepolymers. With the use of capped diamines of this type, these are generally mixed with NCO prepolymers in the absence of water and this mixture is then mixed with the water of dispersion or part of the water of dispersion so that in the interim, the corresponding diamines are released hydrolytically. In this way, it was also possible to add the diamines or polyamines directly to the water.

Other representatives of compounds that can be used as structural components e) in the method according to the invention are described, e.g. in High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology," Edited by Saunders-Frisch, Interscience Publishers, New York, London, Vol. I, 1962, pages 32 to 42 and pages 44 to 54 and Vol. II, 1964, pages 5 to 6 and 198 to 199 and in the Plastic Handbook, Vol. VII, Vieweg-Höchtlen, Carl-Hanser-Verlag, Munich, 1966, e.g. on pages 45 to 71.

The concomitant use of trifunctional or higher functional compounds with groups that can react with isocyanate groups in the sense of the isocyanate polyaddition reaction in small quantities to achieve a certain degree of branching is also possible, as is the possible use of trifunctional or higher functional polyisocyanates for the same purpose that was already mentioned. Also univalent alcohols like n-butanol or n-dodecanol and stearyl alcohol can be used in small quantities.

Preferably, water, diols and triols with low molecular weight of /10 up to 399 can be used as chain-lengthening compounds.

The tertiary amine compound c) is reacted with inorganic or organic acids, so the pH value is in the range of 2.5 to less than 6.5. Basically

all substances are suitable for this that are able to form salts with the tertiary amine after this neutralization reaction. Acids, e.g. hydrochloric acid, acetic acid, fumaric acid, maleic acid, lactic acid, tartaric acid, oxalic acid, sulfuric acid, sulfurous acid or phosphoric acid are especially suitable. Preferably CO₂ (carbon dioxide), formic acid, acetic acid or hydrochloric acid are used. Compounds that have an acid effect can also be used, e.g. anhydrides.

The contact adhesive can advantageously contain up to 30% additives, e.g. tackifying resins like colophonium, hydrocarbon or phenol resins, especially conifer resins (colophonium) and their conversion products obtained by disproportionation, hydration, addition, esterification and polymerization, such as cumaron inden resins, terpene resins, furan resins, ketone resins (like acetone phenone resins, cyclohexanone resins), polyamide resins, terpene phenol resins, alkyl phenol resins, hydrocarbon resins. Instead of finished resin dispersions, the named resins can also be transferred into dispersions by melt emulsification using the polyurethane named under A) with or without further emulsifiers. However, the resins can also be incorporated directly into the prepolymer before dispersion. Also up to 25 weight-% of the following dispersions can be added: homo- and copolymers of acrylates, especially with styrene and vinyl acetate as comonomers, homopolymers and copolymers of styrene, /11 especially with butadiene as comonomer and polychloroprene.

Other additives typical for dispersions include, e.g. preservatives, aging and light protection compounds, inert fillers, etc.

The contact adhesive according to the invention can be manufactured

in a known way. However, it is advantageous to manufacture it in the following steps:

- A) Reaction of the isocyanates a) with the polyols b) and the tertiary amine compound c) to form a polyurethane prepolymer with excess NCO groups;
- B) Reaction of all or only part of the NCO groups of prepolymers with alkoxy silanes d);
- C) Transfer of the alkoxy silane-terminated, and possibly simultaneously NCO-terminated, prepolymers into the aqueous phase by the addition of water that can additionally contain an amine chain-lengthening compound e); and
- D) Adjustment of the pH value by addition of the acids f) to a pH value between 2.5 and less than 6.5, whereby the acid can already be contained in the water from the beginning or may be added to the prepolymer before the dispersion.

The reaction of the isocyanate A) can occur in the presence of an inert organic solvent that is miscible with water, e.g. acetone or N-methyl pyrrolidone. It is removed by distillation after transfer into the aqueous phase C). However, the prepolymers are advantageously manufactured without solvents. The temperature of reaction A) generally lies at 5 to 160°C and preferably at 50 to 120°C.

The prepolymer with NCO groups is reacted, partially or /12
completely, with the alkoxy silane at 50 to 120°C. Preferably only part of the NCO groups is reacted with the alkoxy silanes and another part with chain-lengthening compounds, especially with water.

The alkoxy silane-terminated prepolymers are generally transferred

into the aqueous phase (step C) between 20 and 100°C. Enough water is used so that a 10 to 60, and preferably 20 to 50, weight-percent solution or dispersion of the polyurethanes is obtained. The water can contain a chain-lengthening compound e) and the necessary quantity of acids f). Advantageously, the desired pH value is adjusted at the end.

Manufacturing of the solutions or dispersions according to the invention is not restricted to the method according to the invention, which only represents the preferred way to obtain the products according to the invention. For example, it would also be possible to convert the tert. amino groups present in the NCO prepolymers first by quaternation at least partially into ammonium groups or, instead of using structural components c) having tertiary amine nitrogen atoms, to already use structural components having ammonium groups in manufacturing the NCO prepolymers. In such a case, ultimately polyurethanes would be available that correspond to the data given above with respect to their content of ammonium groups. The term "ammonium groups" thus represents ternary ammonium groups as occur by neutralization of a tertiary amine with an acid and quaternary ammonium groups as are obtained by alkylation of a tertiary amino group.

The solutions or dispersions according to the invention of the /13 cationically-modified, alkoxysilane-terminated polyurethane can be used as such directly for gluing any organic or inorganic substrates. However, preferably up to 30% additive is added to them, e.g. light and aging protection agents, preservatives, resins or resin dispersions and percentages of other non-contact-adhesive dispersion.

The contact adhesive according to the invention can be used as usual (see e.g. Habenicht, "Kleben" [Gluing], Springer Verlag, 1986), i.e. the aqueous dispersion is applied to both the substrates to be connected. Now, the water is removed, whether by evaporation and/or absorption into the materials. Depending on solid content and climate conditions, a flash-off time (minimum drying time) of 10 to 45 minutes is necessary. If the parts to be joined are pressed together during this time, an adhesive bond is obtained with only very low strength or the parts may even slip apart. After this minimum drying time, the strength when pressed together at first increases abruptly, but then drops back down to almost insignificant values at the end of the time (contact gluing time). After this maximum drying time (total of flash-off time and contact gluing time), only low strength is obtained, or even none at all.

With a contact adhesive, it is thus important to precisely comply with the sequence of the contact adhesive time. That is one of the reasons that the discovery of the contact adhesive properties of alkoxysilane-terminated, ionically modified polyurethane dispersions was surprising. In order to determine this, both substrate parts had to be treated with it. In addition, adhesive films that were apparently dry had to be pressed together. Above all, however, the dispersion had to be modified in such a way that an autohesion is possible. /14

The superiority of the contact adhesives according to the invention in comparison to previous water-based contact adhesives is proven by the following measurements:

A 1. Water resistance

In this case, dried adhesive films (thickness: 0.3 mm), after 7 days drying time at room temperature, were aged in water for 48 hours and inspected visually and manually.

A 2. Heat resistance

Beech wood test specimens ($10 \times 2 \times 0.5 \text{ cm}^3$) are overlapped 1 cm (2 cm^2), after 3 days stressed with 1 kg and the temperature was increased by 10°C every 3 hours (starting at 30°C). The temperature at which the test elements resist the stress is designated as heat resistance.

A 3. Initial strength

After a drying time of 30 min (23°C , 50% relative humidity) birch wood test specimens ($10 \times 5 \times 0.5 \text{ cm}^3$) are pressed together with an overlapping surface of 10 cm^2 and a pressure of 0.5 N/mm^2 (20 seconds) and initial strength is determined in a tearing machine 2 minutes after pressing.

The contact adhesives were characterized as follow:

B 1. The storage stability is determined using the following method. Tracking the viscosity of samples in storage at 23°C and 40°C over 3 to 6 months, deviation of less than 25% (related to the initial viscosity) is considered an indication of having storage stability after 3 to 6 months.

B 2. The SiO_2 content is calculated with element analysis using the /15 Si content and/or calculated directly from the quantities of alkoxysilane calculated.

B 3. The concentration of the tertiary amine groups can be derived with the use of components having tertiary amine groups.

B 4. After completed prepolymer reaction, the residual NCO content that is still present is designated as 100%. The subsequent reaction with the

alkoxysilanes reduces this content by a certain percentage. The residual NCO content that is still present can be used after that for chain lengthening in water.

The invention will be explained in more detail using the following examples:

C 1. Manufacturing the adhesives:

The polyols, the dihydroxy and/or diamino amine compounds and the diisocyanates are reacted at 70 to 90°C until the theoretical residual NCO content is obtained. Solvents can be added to reduce viscosity. Then there is a reaction of the alkoxysilane components with a part of the residual NCO groups that are still present until the residual NCO content that is still possible is obtained. Then 40 to 70% dispersion in water, to which the required quantity of acid for neutralization has been added, occurs at this temperature. Amine chain-lengtheners may be added at this point. After a stirring time of approx. 1 hour at 60°C, the dispersion is completed. Concrete data regarding this general specification can be found in Table 1.

C 2. Adhesive bonds:

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The test specimens (10 x 5 x 0.5 cm [sic]) are coated with the adhesive so that a wet film approx. 0.4 mm thick occurs. After approx. 30 to 40 min flash-off time at 23°C / 50% relative humidity, pressing occurs with an overlapping of 2 cm (10 cm²) and a contact pressure of 0.5 N/mm².

C 3. Measurements:

Immediate strengths are determined immediately after gluing (approx. 2 min after that) and end strengths are determined after 3 days by means

of a test machine (Zwick). Peeling values are determined using 90° peeling with the same contact pressure on strips (20 x 2 x 0.5 cm³). The concrete measuring result can be found in Table 2.

C 4. Results:

A comparison of Examples M 1, M 2, M 3 and M5 according to the invention to the other examples shows that the water resistance in comparison to the usual water-based contact adhesives (MO) was improved in every case and the heat resistance was improved in all cases except M 1 and that the initial, final and peeling strengths are equally good (M 5) or better (M 1, M 2, M 3).

Table 1: Components of the composition

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	M0	M 1	M 2	M 3	M 4	M 5	M 6	M 7
Polychloroprene-Basis	Ja	nein	nein	nein	nein	nein	nein	nein
Polyurethan-Basis	nein	Ja	Ja	Ja	Ja	Ja	Ja	Ja
IPDI [val]	/	1,2	1,2	1,0	1,0	0,9	0,5	0,3
TMXDI [val]	/	/	/	0,2	0,2	0,4	0,8	0,8
PTHF 1000 [val]	/	0,48	0,46	0,4	0,2	0,1	0,1	0,5
PTHF 650 [val]	/	/	/	/	/	0,1	0,1	0,1
PPG 1000 [val]	/	/	/	0,05	0,06	0,4	0,8	0,7
AMMO [val]	/	0,013	0,5	/	/	0,1	0,2	0,05
AMEO [val]	/	/	/	0,05	/	/	/	/
SiO ₂ [conv- %]	/	0,24	0,96	0,95	/	1,82	3,84	0,96
Leopoldone	/	/	/	/	/	0,4	0,4	/
N-Methyldiethanolamin	/	0,55	0,54	0,54	0,56	0,4	0,4	/
Acetic acid	/	0,60	0,50	0,54	0,54	/	/	/
DMPA [val]	/	/	/	/	/	/	/	0,2
NaOH [val]	/	/	/	/	/	/	/	0,2
Perchlorperoxyll	55 %	42 %	41 %	60 %	39 %	16 %	37 %	/
pH-Wert	10,5	7,5	5,0	8,5	8,5	9,5	5,0	7,5

Key:

	M0	M 1	M 2	M 3	M 4	M 5	M 6	M 7
Polychloroprene base	Yes	No	No	No	No	No	No	No
Polyurethane base	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes
IPDI [val]								
TMXDI [val]								
PTHF 1000 [val]								
PTHF 650 [val]								
PPG 1000 [val]								
AMMO [val]								
AMEO [val]								
SiO ₂ [weight-%]								
Acetic acid								
N-methyldiethanolamine								
Formic acid								
DMPA [val]								
NaOH [val]								
Solids content								
pH Value								

Table 2: Measuring results

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	M0	M 1	M 2	M 3	M 4	M 5	M 6	M 7 x
Wärmerestfestigkeit	80 °C	50 °C	120 °C	120 °C	40 °C	120 °C	120 °C	-
Wasserfestigkeit ^{xxx}	+	+	++	+	-	++	+++	-
Anfangsfestigkeit [N/mm ²]								
an Holz/Holz	0,5	0,6	0,7	0,6	0,3	0,6	0,3	-
an Holz/PVC	0,5	0,6	0,7	0,8	0,2	0,4	0,5	-
Endfestigkeit [N/mm ²] ^{xx}								
an Holz/Holz	1,6	2,3	2,3	2,2	0,6	1,4	0,7	-
an Holz/PVC	1,8	2,0	2,3	2,3	0,4	1,4	0,6	-
Schälfestigkeit an Leder/Holz [N/cm] SB	18	18	22	25	5	18	7	
Lagerstabilität	gut	gut	gut	gut	gut	gut	gut	schl.

x Coagulates during dispersion

xx Final strength is determined analogously to initial strength, except that the samples are aged not 2 minutes, but 3 days

xxx Water resistance after aging the film 48 h in water at 23°C

+++ = no optical or mechanical changes

++ = films slightly lacking in transparency, relatively good mechanical properties

+ = films have white streaks, obvious negative effects on mechanical properties

- = films largely dissolved in water

Key:

	M0	M 1	M 2	M 3	M 4	M 5	M 6	M 7 x
Heat resistance								
Water resistance xxx								
Initial strength [N/mm ²]								
On wood/wood								
On wood/PVC								
Final strength [N/mm ²] xx								
To wood/wood								
To wood/PVC								
Peeling strength, leather/wood [N/cm]								
Storage stability		good	good	good	good	good	good	no

IPDI = Isophoron diisocyanate
TMXDI = Tetramethyl xylene diisocyanate
PTHF+) = Polytetrahydrofuran
PPG+) = Poly propylene glycol
AMMO = Aminopropyltrimethoxysilane
AME0 = Aminopropyltriethoxysilane

+) the appended number describes the average molecular weight

1. Storage-stable contact adhesive based on an aqueous dispersion or solution of a cationically-modified, alkoxy silane-terminated polyurethane that can be manufactured with the use of the following components:

a) isocyanate with a functionality > 1;

b) polyol;

c) tertiary amine compound with at least one group that reacts with isocyanates in a concentration such that after neutralization with acids, the polyurethane can be dissolved or dispersed in water;

d) alkoxy silane of the general formula $X-Si(-OR)_yH_z$, whereby y stands for 2 or 3,

z stands for 1 or 0,

H = hydrogen or alkyl radical with 1 to 6 C atoms,

X stands for an organic radical that contains at least one group that can react with isocyanate groups and R stands for the same or different radicals of the following group: hydrogen and alkyl group with 1 to 4 C atoms, in a concentration of less than 3.0 weight-percent, calculated as SiO_2 and related to the polyurethane weight;

e) 0 to 20 weight-% chain-lengthening compound, related to the polyurethane weight; and

f) inorganic or organic acids for adjusting the pH value in the range from 2.5 to less than 6.5.

2. Contact adhesive according to Claim 1, characterized by isocyanates with a functionality of 2, especially aliphatic diisocyanates,

e.g. tetramethyl xylene diisocyanate (TMXDI) or isophorn diisocyanate.

3. Contact adhesive according to Claim 1, characterized by /21
polyols with polyester and polyether segments, especially with average
molecular weights MW_n of 100 to 8000, whereby polyether polyols are
preferred.

4. Contact adhesive according to Claim 1, characterized by a
concentration of the tertiary amine compound between 2 and 200
milliequivalents per 100 g polyurethane.

5. Contact adhesive according to Claim 1, characterized in that the
alkoxysilane concentration lies between 0.1 and 3.0 weight-%, calculated
as SiO_2 and related to the polyurethane weight, and preferably between
0.1 and 1.3%.

6. Contact adhesive according to Claim 1, characterized by
chain-lengthening compounds from the following group: water, diols and
triols with low molecular weight of ≤ 399 .

7. Contact adhesive according to Claim 1, characterized by the use
of the following acids: carbon dioxide, formic acid, acetic acid and/or
hydrochloric acid and especially by the use of formic acid.

8. Manufacturing the contact adhesive according to at least one of
Claims 1 to 7, characterized by

A) the reaction of isocyanate a) with the polyol b) and the tertiary
amine compound c) to form a polyurethane prepolymer with excess NCO groups;

B) reaction of the NCO groups of the prepolymers with the
alkoxysilanes d);

C) transfer of the alkoxysilane-terminated prepolymer into the /22

aqueous phase by the addition of water, which can also contain a chain-lengthening compound e); and

D) adjustment of the pH value by the addition of acids f) to a pH value between 2.5 and less than 6.5.

9. Manufacturing according to Claim 8, characterized by the reaction of the isocyanate A) in the absence of an organic solvent miscible with water.

10. Manufacturing according to Claim 1, characterized in that the NCO groups of the prepolymer are partially reacted with alkoxysilanes and partially with water or other chain-lengthening compounds.

11. Storage-stable aqueous dispersions or solutions of a cationically-modified alkoxysilane-terminated polyurethane that can be manufactured with the use of components according to at least one of Claims 1 to 7.